Characterization, Sources and Sinks of Colored Detrital Matter in the Ocean.

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LONG-TERM GOALS

My primary research interest is the effect that phytoplankton community structure has on the optical fields and carbon cycling in the marine environment. Methods used in my lab are based on biomarkers, primarily chlorophylls, carotenoids and their degradation products. These are the chromophores which are responsible for a major fraction of the light absorbed in the ocean. It is my goal to characterize phytoplankton-derived chromophores in the marine environment and determine their effects on ocean optics and access their utility as biomarkers for the study of phytoplankton and processes associated with these in the ocean.

OBJECTIVES

The optical properties of the ocean are primarily determined by the optical properties of water, particles and dissolved matter. The absorption of light by particles is due to phytoplankton and colored detrital matter (CDetM). Whereas the chromophores associated with phytoplankton have been studied extensively over the last 50 years, little is known about chromophores associated with CDetM. An independent study of these is warranted as CDetM can contribute significantly to the absorption of light in the coastal zone and as concentrations of CDetM are not expected to covary with phytoplankton biomass. The project is a study of the nature and the sources and sinks of CDetM in the water column. The study's objectives are:

1. Characterize the chromophores of different classes of detrital matter, i.e., fresh and partially degraded fecal matter, resuspended sediments, particulate matter from below the euphotic zone and living organisms devoid of phytoplankton-derived pigments.
2. Search for specific chromophores that uniquely identify the different classes of detrital matter such that these marker-chromophores can be used to identify contributions of different classes of detrital matter to CDetM in the upper ocean.
3. Develop methods for the routine analysis and characterization of chromophores associated with CDetM.
4. Determine photo-degradation rates and microbial-degradation rates of different detrital chromophores in order to understand the dynamics of these compounds in the upper ocean.

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APPROACH

As potential sources of CDetM, extracts of phytoplankton, zooplankton, sediments and fecal material is subjected to chemical tests to identify and characterize the major chromophores associated with these. To characterize sinks, selected material is subjected to controlled microbial degradation and photooxidation. These experiments will delineate the relevant time scales for these compounds in the water column as a function of temperature and light.

WORK COMPLETED

Work to date has focused on 1. characterizing the chromophores associated with sediments from a variety of locations and fecal matter of diverse micro- and macrozooplankton, 2. developing methods for the extraction of chlorophyll degradation products from sediments and fecal matter, and 3. studying the changes of sedimentary chromophores when anoxic sediments are resuspended in oxygenated water.

RESULTS

We recently discovered in sediments a new class of Chl *a* degradation products, carotenol chlorin esters (CCEs). Chlorins associated with these were identified as pheophorbide *a* and pyropheophorbide *a*. The carotenols are isofucoxanthin-5'-dehydrate and isofucoxanthinol-5'-dehydrate, compounds uniquely derived from fucoxanthin, a biomarker for diatoms. CCEs were only found in the fecal matter of copepods grazing on diatoms, not in the fecal matter of microzooplankton grazing on flagellates. Based on these results it is hypothesized that CCEs are a sedimentary biomarker for diatoms.

The distribution and sources of the chlorin 13^2, 17^3-cyclopheophorbide *a* enol (CCP517) were studied. An analytical system for its quantification in sediments was developed. It was found that CPP517 contributes 30 to 70% to the sum of the identifiable chlorins. It was shown that even though CPP517 is very labile in organic solvents it is fairly stable when associated with sedimentary particles. It is probable that CPP517 associated with sediments is stabilized by complexation with metals. CPP517 is produced by all marine herbivores we have studied to date, i.e., diverse protozoans, the copepod *Calanus pacificus*, the euphausid *Euphausia* sp. and salps, contributing 25 to 60 % to the sum of all chlorophyll a (Chl *a*) degradation products. A series of other cyclic pheophorbides based on divinyl Chls *a* and *b* and on Chls c_1 and c_2 was discovered. Analysis of CPPs in material collected in sediment traps in the Eastern Tropical North Pacific allowed us to deduce that *Prochlorococcus* contributes significantly to export fluxes of pigments, and by implication carbon, in that environment.

The marine cyanobacterium *Prochlorococcus marinus* contributes significantly to phytoplankton biomass and primary production in the subtropical and tropical open ocean. Its major pigments were characterized previously, its minor pigments were characterized as part of this project. The Chl *c*-like pigment found previously in *Prochlorococcus* was identified as 2, 4 divinyl Mg-pheoporphyrin a_5 methyl ester. Deep populations of *Prochlorococcus* were found to have high concentrations of a pigment likely to be parasiloxanthin, a pigment previously only found in the Common Japanese Catfish. Parasiloxanthin is derived from zeaxanthin and might be used by *Prochlorococcus* to fine-tune membrane fluidity as the ambient temperature varies.

Anoxic sediments from the Peru margin were resuspended in oxygenated and deoxygenated seawater for periods ranging from 50 to 250 hours. Concentrations of chlorins were followed over

time. No significant decrease of pigment concentrations occurred. However, a 2 to 3 fold increase in concentrations of chlorophyllone was observed in the oxygenated treatment but not the deoxygenated treatment. It is possible that chlorophyllone was tightly bound to the sedimentary matrix under anoxic conditions but that the bonding was weakened under oxic conditions. Consequently it was easier extracted into organic solvents.

IMPACT / APPLICATIONS

The discovery of high concentrations of chlorin-carotenol esters and cyclic pheophorbides in marine sediments and herbivore fecal material requires a rethinking of the diagenesis of Chl *a* in the marine environment. The data show that changes to the isocyclic ring of Chl *a* occur very early during diagenesis. The presence of high concentrations of CPP517 in the marine environment, which unlike other Chl *a* degradation products has a major absorption band at 690 to 720 nm, will have a significant impact on the optical properties of detrital matter in the ocean. This may affect the use of near-IR bands associated with optical sensors.

TRANSITIONS

The work is fundamental to ocean optics and biological/chemical oceanography; there are no expected transitions at this point. The implications of the work, however, may affect the interpretation of near-IR optical bands in the marine environment.

RELATED PROJECTS

The activities of this project are related to those of Greg Mitchell who studies the optical properties of the California Current system.

PUBLICATIONS:

Amy Shankle, Ralf Goericke, Lisa Levin, 1998, Possible productivity variations in the Arabian Sea over the last millennium deduced from concentrations of Chl *a* degradation products in sediments. Abstract for a talk at the AGU 1998 Ocean Sciences Meeting, San Diego, USA.

Goericke R., A. Shankle, D. J. Repeta, Novel carotenol chlorin esters from marine sediments and water column particulate matter, Subm. to Geochim. Cosmochim. Acta.

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Goericke R., R. Olson, A.Shalapyouok, A novel niche for *Prochlorococcus* sp. in low-light suboxic environments in the Arabian Sea and the Eastern Tropical North Pacific. Subm. to Deep Sea Research I.

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